3725

Grafting of Vinyl Monomers on to Proteins

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ONE of the basic methods of modifying the properties of proteins and other polymers is the synthesis of graft copolymers based on them. Grafting of vinyl monomers to natural and synthetic polymers has been suggested as a potentially effective means of altering the properties of the base polymer[1]. Our knowledge on the grafting of vinyl monomers on to proteins is very scanty compared to that on the grafting of monomers to starch, cellulose and other polysaccharides. The relevant literature remains scattered and by present-day standards is not voluminous. In this review, an attempt has been made to present in one place as much as possible of the comparatively sparse literature on the different techniques adopted to graft vinyl monomers on to various proteins. Progress in the field of grafting of vinyl monomers on to starch, cellulose, etc., has been extensively reviewed by different workers[2-5] in recent years and several recently published books[6-13] contain excellent reviews in the general field of grafting by radiation and chemical methods. The various methods of grafting of block and graft copolymers and their physico-chemical characteristics have been recently reviewed by Prabhakara Rao and Santappa[14] and Shah and Subramanian[15]. Though several methods of producing such graft copolymers are available and the field is expanding rapidly, the number of potential catalysts for graft copolymer treatments of proteins is limited. These techniques as applied to proteins are briefly reviewed below.

Free Radical Initiated Graft Copolymerization of Vinyl Monomers

Grafting by Irradiation of Polymers

High energy irradiation methods — There are two different approaches to radiation grafting[16]. These are usually referred to as mutual and pre-irradiation methods. The mutual technique involves irradiating the substrate in the presence of the monomer in liquid or vapour phase. In general, the applicability of this method is limited to systems in which the radical yield from the substrate polymer is higher than that from the monomer; otherwise, excessive homopolymerization results. The pre-irradiation methods involve irradiating the substrate alone and then bringing it in contact with liquid or gaseous monomers. Grafting takes place by the reaction of the monomer with the trapped radicals. Most of the monomers can be grafted by this technique. The mutual method gives homopolymers, whereas the pre-irradiation method gives mainly true graft copolymers[16].

Both the methods have been successfully employed for the grafting of vinyl monomers on to wool[17-24] and silk[25]. In two recent patents, the grafting of vinyl monomers on leather and skins is described[26,27]. The grafting experiments were carried out in the presence of wetting agents and penetrators and the emulsion exposed to 100,000-250,000 rads radiation from a ^{60}Co source. Some of the grafted samples showed decrease in water absorption and increase in resistance to degradation in moist hot bed. Acrylonitrile (AN) grafted samples were also resistant to bacteria and fungi[26,27].

When ionizing radiation is used for grafting a monomer on to a protein, the sensitivity of the protein towards high energy irradiation is an important factor. Although protein fibres would be progressively damaged with increasing radiation dose, it was observed[28] that there was no appreciable damage in the case of wool fibres when the radiation dose was less than 5 million REP (roentgen equivalent physical). Hence, radiation to this extent can be used safely to catalyse polymerization reactions in wool.

In recent years, a number of reports on the action of gamma irradiation on native collagen have appeared, which show that gamma irradiation may have a degrading effect on collagen[29,30]. Little[31] reported that the crystalline areas of collagen become disordered at relatively low doses of irradiation compared to silk, keratin and other proteins. Bailey *et al.*[32] also reported a progressive decrease in the hydrothermal shrinkage temperature with increase in dose when collagen fibres in normal saline solution at 0°C are exposed to ionizing radiation up to 40 Mrad. The value dropped from 61° to 47°C on increasing the dose beyond 5 Mrad and it was about 25°C beyond 40 Mrad dose. These values are in agreement with the values given by Cassel[33] for kangaroo tail fibres. The results, therefore, indicate the necessity for caution in using gamma irradiation for the grafting of vinyl monomers on to native collagen. The method may, however, be suitable for grafting on to gelatin and the degradation products of collagen.

Radiation polymerization has the advantage of instantaneous production of initiating radicals, limited dependence of initiator upon temperature, freedom from catalysts and their residues, uniform production of radicals throughout the system and better control of the polymerization reaction.

Low energy irradiation in the presence of sensitizers — The low absorption energy from ultraviolet irradiation can be advantageously utilized for the grafting of vinyl monomers on the proteins; in this type of irradiation, degradation of the substrate is almost negligible. The yield of the graft copolymer can often be increased by using an ultraviolet sensitive dye[34] or other photosensitizers to activate the process. Ultraviolet light may also be used to introduce hydroperoxide groups into the backbone polymer by irradiating in the presence of air[35] and following the treatment by redox initiated graft copolymerization. Ultraviolet-induced crosslinking and grafting on solid high polymers, including

proteins, have been studied by Oster and co-workers[35,36]. In the treatment of proteins the mechanism was not defined, but the method was said to be applicable to keratins, collagens, silk, hair and leather. Recently, Ishibashi and Oku[37] have utilized this technique for the photochemical graft copolymerization of styrene on to wool.

Needles[38,39] and Needles and Wasley[40] reported the riboflavin sensitized photopolymerization of low concentrations of aqueous acrylic monomers in the presence of proteins like wool, silk and collagen or amino acids. He obtained evidence of grafting by extraction methods and enzymatic digestion of the protein backbone from the graft copolymer and the physical mixture of gelatin and homopolymer. Chemical and physical characterization of the protein-polymer products revealed that only a small number of initiation and grafting sites were present in the protein. It was suggested that these photopolymerizations proceed via a free radical pathway involving abstraction of hydrogen from the protein by dye intermediates.

Grafting of methyl methacrylate (MMA) on to collagen using benzoquinone as a photosensitizer has been recently reported by Kudaba *et al.*[41]. Grafting was carried out by adding 5% benzoquinone to collagen, then mixing collagen with aqueous solution of MMA in the ratio 1:2, and irradiating the mixture with quartz lamp. The ungrafted homopolymer was washed out with acetone and the amount of MMA in the graft copolymer was obtained from its nitrogen content as compared to that of collagen. The influence of a number of factors on the extent of grafting was also investigated by them.

Chemical Redox Methods

Potassium persulphate method — Madaras and Speakman[42] illustrated the use of persulphate in initiating graft copolymerization in proteins. They found that when wool was treated with persulphate and methacrylic acid at 25°C for 1 hr, large amounts of polymer were formed. Lohani *et al.*[43] polymerized acrylonitrile in wool using persulphate as initiator within a short time in the presence of air. Persulphates altered the mechanochemical properties of wool, e.g. set, super-contraction, to a much greater extent than the hydrogen peroxide-ferrous ion initiator system. Wolfram and Speakman[44] discussed the mechanism of initiation of polymerization of acrylonitrile within wool fibres. They questioned the validity of the hypothesis that polymerization was initiated within the protein by free radicals by the action of persulphates on cystine and put forward the hypothesis that polymerization was initiated by a different mechanism. They concluded that the persulphate ion concentration inside the fibres greatly exceeded that in the surrounding solution and thus free radicals were formed preferentially inside the fibres ($S_2O_8^{2-} \rightarrow 2SO_4^{\cdot -}$), leading to preferential internal deposition of the polymer[44]. It was shown by the same workers[44] that acrylonitrile can be polymerized readily within the regenerated protein fibre (fibrolane), but not in wool, in which basic groups have been blocked nor in wool which has been oxidized by peracetic acid using persulphate initiation technique.

Casein[45-49] has been modified by persulphate-catalysed polymerization with various vinyl compounds, but whether a graft copolymer was obtained or not is not clear.

Recently, Wolfram and Menkart[50] found that the deposition of vinyl polymers in wool can be accomplished in the presence of air using tetrakis-hydroxymethyl phosphonium chloride (THPC) as an oxygen scavanger in persulphate initiated polymerization. The principal variables of the process, like initiator concentration, THPC concentration, monomer concentration, etc., and the properties which may be imparted to wool were mentioned. The above method was successfully utilized in polymerizing acrylonitrile on to collagen, but this method was found to be unsuitable with other vinyl monomers (Panduranga Rao, K., Thomas Joseph, K. & Nayudamma, Y., unpublished work). Khismattullina *et al.*[51] and other workers[52] used the potassium persulphate initiation technique to synthesize graft copolymers of gelatin and vinyl monomers. They presumed that the graft copolymer was formed by radical polymerization at active centres formed on the gelatin molecule by chain transfer.

Although persulphate has been used to initiate free radical polymerization of acrylates on wool, little is known of the nature of the attack by persulphate on wool protein. Needles[53-55] reported that the cystine, tyrosine and methionine residues on wool and silk are easily attacked with persulphate. Persulphate is known to yield sulphate and hydroxyl free radicals on thermal decomposition in aqueous solution. In the presence of an oxidizable substrate, induced free radical decomposition occurs[56,57].

$$\tfrac{1}{2}S_2O_8^{2-} \xrightarrow{H_2O} SO_4^{\cdot -} \longrightarrow OH. + HSO^-$$

$$X{-}H \xrightarrow[\text{or } OH.]{SO_4^{\cdot -}} X. + HSO_4^- \quad \text{or} \quad H_2O \xrightarrow{S_2O_8^{2-}} X{-}OSO_3^- + SO_4^{\cdot -} \rightarrow \text{etc.}$$

where X—H denotes the oxidizable substrate.

Needles[57] presumed that peroxydisulphate attack on gelatin occurs via such an induced free radical decomposition forming reactive groups in gelatin that are capable of crosslinking or degradation.

Silver persulphate initiation[58] cannot be easily confined inside the wool fibres, since the persulphate ion breaks down at a significant rate even in the absence of silver ions to form free radicals in the monomer solution which produces homopolymers.

Ferrous ion-hydrogen peroxide method — It is presumed that polymerization is initiated on the wool molecule in the presence of ferrous ion-hydrogen peroxide system as a result of the formation of R—S· radicals derived from initiation attack at the disulphide bonds[59-61]. The ferrous ion-redox system has been applied successfully for the grafting of a number of polymers on to wool, viz. methacrylic acid[62], methacrylamide[42], vinylidene chloride[61], methyl and ethyl acrylate[63] and methyl[62,63], ethyl and *n*-butyl[63] methacrylates, as well as copolymers prepared from the mixtures of these monomers.

Recently, the ferrous ion-peroxide system of Lipson and Speakman[62] was used to graft acrylic acid and AN on wool by Leeder *et al.*[64] to study the effect of vinyl polymers on water absorption in particular. D'Arcy *et al.*[65] studied the influence of some factors on the yield of polyacrylonitrile polymerized *in situ* within wool fibres by means of the ferrous ion-hydrogen peroxide initiator system.

Recently, Kudaba and Ciziunaite[66,67] used the ferrous ion-hydrogen peroxide redox system to graft acrylamide (AA), AN and vinyl acetate on to collagen. Collagen powder was pretreated with ferrous ammonium sulphate solution and then treated with aqueous solutions or emulsions of the monomers and hydrogen peroxide. The homopolymers formed were removed by extraction with suitable solvents. The optimum conditions of grafting varied from monomer to monomer. The percentage of grafting increased significantly at elevated temperature (60-70°C) in the case of acrylamide and acrylonitrile, but in the case of vinyl acetate maximum grafting was achieved at low temperature. It is, however, likely that collagen may undergo denaturation at the higher temperatures used by Kudaba and Ciziunaite[66].

Hydrogen peroxide is known to react with wool, causing rupture of disulphide and peptide bonds[68] and the reaction is greatly catalysed in the presence of heavy metal ions[69]. Deasy[70,71] and Deasy and Ernst[72] have shown that metal ion-hydrogen peroxide systems attack collagen, solubilizing it at room temperature even at low concentrations of hydrogen peroxide and metal ions. It was found that low concentrations of Cu^{2+}, Fe^{2+}, Cr^{3+} and $Cr_3O_7^{2-}$ (but not Ce^{4+}, Ni^{2+} or Mn^{2+}) in the presence of hydrogen peroxide cause complete or partial solution of steer hide corium collagen at room temperature. It is, therefore, doubtful whether all the metal ion-hydrogen peroxide systems can be utilized for grafting on to collagen without degrading its native structure.

Ceric ion technique — Ceric salts are capable of oxidizing a large number of organic compounds, such as alcohols, aldehydes, amines and thiols[73] and producing free radicals which may initiate polymerization. The system most studied is that comprising Ce^{4+} and an alcohol, which react as follows:

$$Ce^{4+} + RCH_2OH \rightleftharpoons \text{Complex} \rightarrow Ce^{3+} + H^+ + \dot{R}CHOH \text{ or } (\dot{R}CH_2O)$$

It is not certain whether the hydrogen is abstracted from a carbon or from the oxygen atom. At any rate, radicals are produced on the polymer and monomers can be grafted thereon. It is only in the last few years that this reaction has been exploited for this purpose, notably by Mino and coworkers[74-78] and by several other investigators[79-83]. Most of this work has been on the modification of cellulose fibres, but the technique is of wide applicability. This method of grafting has been extremely effective with polyvinyl alcohol (PVA), partially hydrolysed polyvinyl acetate and starch as polymeric backbones for obtaining grafts with several vinyl monomers. However, very little information is available on the grafting of vinyl monomers on to proteins using the ceric ion technique. This technique has been recently employed by several workers[84-87] for the grafting of certain vinyl monomers on collagen. The influence of different factors, such as time, temperature, monomer concentration, ceric ion concentration, etc., on the content of graft has been investigated. The concentrations of the monomer and the catalyst are important factors influencing the percentage of grafting[85]. The rate of diffusion of the monomer into collagen also appears to be an important factor affecting the degree of grafting and this factor is dependent upon the state of collagen; swollen and solubilized collagen grafts more of the monomers than insoluble collagen. To establish the proof of grafting unequivocally as opposed to an intimate mixture where no primary chemical bonds exist between collagen and the polymer, several lines of evidence were sought. The different lines of evidence obtained in this study indicated that the copolymers obtained by ceric ion initiated free radical polymerization of vinyl monomers on collagen are not physical mixtures of collagen and the homopolymer. Indications that these products are true grafts are provided by the solution properties of the isolated products, their general behaviour in respect of swelling in different solvents and also by the infrared spectra of the isolated grafts. Graft polymerization of MMA on a number of modified collagens was also studied[87] in order to elucidate the mechanism of the oxidation of collagen and to determine the grafting sites on collagen using the ceric ion technique. The data obtained on the grafting of vinyl monomers on different modified collagens did not provide any unequivocal proof on the nature of the functional group involved as the grafting site. The number of grafting sites obtained in the case of unmodified collagen indicated that the grafting reactions involved only a small proportion of the collagen molecules. However, the general trend of the results obtained with modified collagen samples indicated that hydroxy amino acid residues and the peptide backbone of the protein may provide sites for the initiation of the grafting reaction.

Recently, graft copolymerization on to proteins by the ceric ion method has been reported by Iwakura and Imai[88,89]. Methyl methacrylate and acrylamide were grafted on to ovalbumin and the graft copolymerization was extremely rapid and seemed to be complete within 5 min under the conditions adopted. It was indicated from the studies on the grafting site, that the carbohydrate residue is a possible grafting site on ovalbumin. The results of grafting experiments revealed that only a limited part of ovalbumin participated in grafting. In the case of bovine serum albumin (BSA)[89], the number of grafting sites was found to be only 0·02-0·3 mole/mole using the ceric ion method. Denaturation of the protein molecule affected the grafting reaction to a great extent. The most probable grafting sites on BSA were assumed to be the cysteine and cystine residues.

Recently, Sugiyama and Murase[90] and Song *et al.*[91] reported graft copolymerization of AA and methacrylamide on to silk using the ceric ion technique. The effect of various factors like monomer

concentration initiator concentration, reaction period, temperature and *p*H of the reaction system on percentage grafting was studied. By comparing the solubilities in Schweitzer's reagent and from the infrared spectra of silk and grafted silk, it was shown[91] that a true graft copolymer was formed. The dry crease recovery of grafted silk increased with percentage grafting, but the wet crease recovery of grafted silk did not change[91].

Recently, several other redox systems have been tried for grafting studies. The following initiators deserve mention in this connection: Mn^{3+} (ref. 92, 93), V^{5+} (ref. 94-96), Ti^{3+} (ref. 97), the uranyl cation[98,99] and the periodate[100,101] and bromate anions[102]. Sadova and Konkin[96] recently reported the grafting of vinyl monomers to wool keratin using vanadium (V^{5+}). The effect of reaction period, temperature and the concentrations of HVO_3, H_2SO_4 and the monomer on graft copolymerization of wool with AN, MMA and acrylic acid was studied. The mechanism of graft copolymerization was studied on model systems to elucidate the grafting sites on wool using AN and MMA and various amino acids. It was concluded that the S—H groups of cysteine and indole NH groups of tryptophan present in wool take part in graft copolymerization.

Of the known initiators available for grafting, the ceric ion-redox system appears to be the best initiator for grafting on proteins, since in this case, the backbone substrates are degraded to the minimum extent and the formation of homopolymer is also negligible. However, some of the other redox systems, such as Mn^{3+}, V^{5+}, Ti^{3+}, etc., are only of recent origin and further work is necessary to make a critical assessment of the usefulness of these initiators for grafting on proteins.

Lithium bromide-potassium persulphate method — Negishi *et al.*[103,104] found that the aqueous redox system containing bromide and persulphate ions can be utilized effectively for the graft copolymerization of various acrylates in wool fibres at a relatively low temperature and without homopolymerization. Grafting was more effective with reduced wool than with untreated wool. The initiation of graft copolymerization in the bromide-persulphate redox system is presumed to be through the formation of free radicals by the following reaction[104]:

$$Br^- + S_2O_8^{2-} \rightarrow Br. + SO_4^{\cdot -} + SO_4^{2-}$$
$$SO_4^{\cdot -} + H_2O \rightarrow HSO_4^- + OH$$
$$Br + Br \rightarrow Br_2$$

Thus, radicalotropy to thiol groups on wool from the sulphate ion and the hydroxyl and/or bromide radicals might occur.

The grafting of vinyl monomers to skin[105], gelatin[106,107], casein[47-49], zein[108,109], soyabean protein[110] and certain inedible proteins[111] using certain redox systems is described in a number of patents.

Anionic Initiation

There are a number of monomers which cannot be polymerized by free radical initiators, but which do polymerize under ionic conditions. Krull and Friedman[112] investigated the anionic graft copolymerization of methylacrylate (MA) to a variety of model compounds and to wheat gluten in dimethyl sulphoxide (DMSO) in the presence of sodium hydride. Initiation proceeded by an anionic mechanism and the rate determining step was the production of the initially formed carbanion. Studies on several series of model compounds containing the functional groups present in proteins and amino acid analysis indicated that the functional groups of amino acids like histidine and arginine as well as cysteine and tyrosine and the peptide bonds were acting as the initiation sites in proteins. The functional groups of threonine, serine and lysine were also involved to a great extent. With both the model compounds and the proteins, polymerization was initially rapid and then levelled off, although the rates depended on the concentrations of the activator and the acrylate.

Aqueous Emulsion Grafting Technique

Because many of the vinyl esters have limited water solubility, an emulsion polymerization technique has great practical significance. Ishibashi and Oku[113] carried out aqueous emulsion graft polymerization of styrene to wool. The effects of the type of initiator used, temperature and period of grafting on the extent of grafting were examined. The rate of grafting increased with increase in grafting period and temperature. Benzoyl peroxide was found to be more effective than potassium persulphate and a mixture of nonionic and anionic surfactants was more promising as an emulsifier compared to other surfactants. Simpson and Vanpelt[58] tried to graft AN to wool using an emulsion technique by the catalyst *bis*-acetonyl acetonato copper^{2-}-trichloroacetic acid [$Cu(acac)_2$-TCA], but failed.

The aqueous solution technique followed for the grafting of vinyl monomers on to collagen powder and collagen solution was found to be unsuitable for grafting on to the three-dimensional network structure of pelts (hide collagen). Panduranga Rao[114] was able to successfully graft various vinyl monomers on goat skins using the ceric ion aqueous emulsion technique. However, the choice of the emulsifier for the synthesis of graft copolymers with the salts of Ce^{4+} is very limited. The emulsifier used must not be oxidized by Ce^{4+}. Otherwise, the polymerization of the monomer would be initiated by the system emulsifier-Ce^{4+} with the formation of a homopolymer.

The omission of an additional emulsifier is a critical factor, since the emulsifier would favour homopolymerization rather than graft copolymerization. To prevent excessive homopolymerization of the added monomer the amount of the additional emulsifier should be kept minimum. Too much emulsifier leads to the formation of micelles in the aqueous phase and this generates normal emulsion polymerization[115].

Vapour Phase Technique

Radiation grafting of vinyl monomers on to wool and silk has been studied by Armstrong and Rutherford[19] using a mutual vapour phase

technique. Gagliardi *et al.*[116] recently observed that all MMA vapour grafted cotton samples using the ceric ion technique were very soft, indicating that no fibre cementing had occurred due to the presence of the polymer. The method of grafting in monomer vapour has several unique features — the amount of the homopolymer produced is small, and the separation and purification of the graft copolymer is easy. In many cases, it is also possible to get a high degree of grafting compared to other methods.

Newer Types of Catalysts for Graft Copolymer Formation in Protein Fibres

Simpson and Vanpelt[58,117] and Simpson[118] developed a new method for the initiation of graft copolymerization of AN inside the wool fibre using as catalysts the adducts formed between the *bis*-(acetonyl acetonato) copper^{2-} and ammonium trichloroacetate or trichloroacetic acid. The effects of various factors like temperature, initiator concentration, monomer concentration and water on grafting rates were studied. On the basis of these results, it was suggested that polymerization may be brought about by a combination of the ionic and free radical mechanisms.

Initiation of free radical polymerization by metal carbonyl-organic halide systems was extended by Bamford *et al.*[119] to the case in which the halide component was a N-halogenated amide or alkylamide. If the overall process of initiation followed the familiar course with these halogen compounds, the primary radicals would have the structure $RCONR^1$. Since N-halogenated amides can be prepared from polyamides and polypeptides by direct halogenation[119], these results appeared to provide the basis for a convenient method of grafting on to these substances. Grafting on to nylon, wool, silk and gelatin was indeed readily effected by this method[119].

The carbonyl system proved to be more efficient than many free radical systems[120]. The carbonyl system yielded free radicals very quickly at room temperature. Initiation by cobalt carbonyl and carbon tetrachloride was almost 10,000 times as fast as initiation by alpha, alpha^1-azodiisobutyronitrile (AZDN) at 25°C (ref. 121). The carbonyl system can affect the structure of the polymers produced; polymethylmethacrylate with nickel carbonyl initiator has a higher isotactic content than the product of the conventional free-radical polymerization[121]. Thus, there are differences in speed of polymerization and the nature of polymer produced, which could conceivably be exploited.

Factors Influencing Graft Copolymerization

Diffusion — The importance of diffusion in graft polymerization reactions has been discussed in detail by Chapiro[8]. There must be sufficient monomer available for the active centres produced by irradiation to initiate chain formation before termination. The diffusion of the monomer into the protein fibres is the most important factor governing the degree of grafting, and this factor is dependent upon the polarity of the monomer, the state of the protein structure, the reaction temperature, and the presence of solvents and diluents.

Effect of pH — A definite pH is required to carry out certain polymerization reactions; pH may affect the rate of graft polymerization in two ways: (i) by tending to coagulate the dispersed phase, and/or (ii) by affecting the rate of the initiating process.

Wolfram and Menkart[50] in grafting vinyl monomers to wool found that in this system, successful internal polymer deposition could be obtained only within a relatively narrow pH range. Simpson and Vanpelt[58] observed very few polymer initiation reactions to occur until the solution had reached pH 5 or higher; pH has got a definite effect on the ceric ion initiation technique. The optimum pH was found to be 2·1 in the case of grafting of vinyl monomers to collagen; at higher pH values the efficiency of grafting decreases and there is almost no grafting above pH 3·5 (ref. 114). The pH dependence might be interpreted as being due to the fact that the rate constants of both initiation (K_i) and termination (K_t) are affected by the amount of acid added. It may be probable that at pH values higher than about 2·1, increase of K_i with acid addition is more rapid than that of K_t, while this relation is reversed at lower values.

Solvent medium — It is important to select the most suitable solvent for graft polymerization to protein fibres. The effect of water in enhancing the grafting of vinyl monomers on to hydrophillic polymers has been reported by Huang and Rapson[122], Chapiro and Stannett[123] and Stannett and Hoffman[124]. Chapiro and Stannett[123] explained this phenomenon on the basis of the swelling effect which enhances diffusion into the polymer film. Stannett *et al.*[20] reported that water and/or methanol are necessary for efficient grafting of vinyl monomers, as they help in the diffusion of monomers to the active centres created in wool by irradiation. Simpson and Vanpelt[58] found that swelling of the wool fibres in a substantially aqueous system or minimally a lower alcohol are very desirable in achieving significant grafting. Ishibashi and Oku[113] observed very little grafting on to wool in the absence of a solvent. Swelling agents like N,N-dimethylformamide and dimethylsulphoxide were found ineffective. This may probably be due to the readiness of chain transfer from the graft copolymer radical and the wool backbone radical to the solvent as a result of which the growth of the graft chain does not proceed further. The same trend of results was observed by Fanta and coworkers[125,126] in the case of grafting of AN to starch using ceric ion in the presence of dimethylformamide. However, in proteins the presence of water or methanol was found necessary for efficient grafting; especially with monomers of low polarity selective additives are needed to increase the solubility and the rate of diffusion of the monomers to the active sites without destroying them.

Surface active agents — Surface active agents have been used in polymerization reactions to start the reaction and to increase the rate of reaction in the same way as catalysts[127]. The types of surface active agents and their charge may affect the degree

of polymerization. In general, cationic surfactants are used less frequently for acrylic emulsion polymerization. Many vinyl monomers may be polymerized in an aqueous emulsion (prepared with a small percentage of the fatty acid soap or detergent) containing a water-soluble source of free radicals.

Inhibitors and retarders — Various substances can reduce the rate at which a monomer is converted to a polymer. Inhibitors completely suppress polymerization, while retarders reduce the rate of polymerization. Inhibitors react very readily with the primary radicals to give unreactive products, so that the growth of the polymer chains cannot begin. The inhibitor is gradually consumed and ultimately polymerization starts. Inhibitors like hydroquinone are commonly used to stabilize monomers during storage. Retarders are, in general, less reactive than inhibitors; the additive reacts with the radicals only after some monomer units have been added to the primary radical, so that polymerization is not completely stopped.

Many investigators[128-131] observed that molecular oxygen was a strong inhibitor of aqueous or emulsion graft copolymerization. In peroxydisulphate[132], peroxide, and H_2O_2-metal ion[133] and ceric ion-redox initiation system[134], the presence of oxygen has an inhibiting effect on the aqueous and aqueous emulsion polymerization of many monomers. The instability of the free radicals in oxygen atmosphere in many cases limits the utilization of the graft polymerization technique on an industrial scale. Careful engineering is also required to eliminate the introduction of impurities or contaminants which may inhibit or retard graft copolymerization. Metal ions[135] and the sulphur compounds found in rubber tubing[136] may also inhibit the polymerization reactions. Of the common metals only aluminium was found not to be injurious. Hydroquinone[137,138] and nitrobenzene[139-143] and other aromatic nitro compounds were found to retard graft copolymerization. Burke *et al.*[17] reported that the free radicals produced when wool is irradiated by gamma rays are stable only in the absence of oxygen. The radicals decay almost as rapidly as they are formed in air. Lohani *et al.*[144] found that oxygen acts more as a retarder of the reaction than as a complete inhibitor in grafting wool using ammonium persulphate initiator. Although higher yields are obtained in nitrogen, adequate polymer yields are obtained even in air.

Pretreatment — The function of pretreatment is twofold: (1) removal of the foreign materials such as wax or grease from the surface, and (2) modification of the fibre surface. Microscopic examination has shown[145] that pretreatment of wool fibres assists the spreading of preformed polymers on the surface of the fibres, and thus enables the desired properties to be obtained with only small amounts of the polymer (1-2%). The pretreatment conditions and the compound used for pretreatment also affect the polymerization reactions.

Valentine[61] has shown that the type of wool used and the pretreatment history of the wool have a marked influence on the deposition of polymers inside the fibres. In grafting of vinyl monomers on to pelt (hide collagen) the removal of wax or grease was found necessary[114]. Wax or grease may hinder the diffusion of monomer into the pelt in some way, and hence the removal of natural grease from its interfibrillary spaces enables more even penetration and action of monomers.

Physical state of the substrate — The physical state of the substrate[89,146] (whether swollen or faccid) and its compactness, the availability and accessibility of the reactive protein groups of different types, the polarity of the monomer and the number of grafting sites available in the various functional groups are important factors influencing the degree of polymerization and the distribution of vinyl polymer in the protein structure.

Backbones Especially Susceptible to Chain Transfer

It is often convenient to modify the structure of the backbone polymer to favour the chain transfer step leading to graft formation. The data available in the literature[147,148] indicate that carbon-halogen and sulphur-hydrogen bonds are more susceptible to radical attack and transfer than carbon-hydrogen bonds and by incorporating halides or mercaptans into the backbone, the ratio of the chain transfer to chain propagation, on which the efficiency of the grafting process depends, may be favourably altered.

Functional groups, not present in the original protein, can also be introduced through chemical modification of the protein and grafting can be accomplished through such groups. For example, vinyl groups can be introduced in proteins by reaction with maleic anhydride[149], acrylyl chloride[149], etc., and polymerization of vinyl monomers in the presence of the vinylated protein should establish graft copolymerization. This method has been used by Speakman and coworkers[150,151] in the case of wool. Reaction with isocyanates[152] is also known to introduce into proteins groups which will subsequently take part in the polymerization reaction.

The presence of chemical groups on modified cottons could offer sites for increased interaction of monomers with cellulose upon high energy radiation. When cotton was modified by cyanoethylation, the presence of cyanoethyl groups offered sites for enhanced interaction with monomers upon high energy radiation[153]. The extent of interaction was dependent on the degree of substitution of the cotton and the radiation dosage. The number of grafting sites in collagen was also found to be significantly increased when collagen was modified by vinylation, thiolation, bromination and cyanoethylation[87]. Such modified collagens may serve as useful substrates for studying the mechanism of grafting and to improve the efficiency of grafting on collagen.

Conclusion

Graft copolymerization reactions have opened new lines of approach for improving the properties of several natural polymers. From the trends in other industries, such as rubber and textiles, it would appear that leather will be largely replaced by synthetics. Man-made materials have slowly

been invading the markets traditionally held by leather. Synthetics have invaded the sole leather and insole fields and the Dupont Company has carried out a carefully planned research programme to replace shoe upper and garment leather. This development poses a serious threat to the continued profitable utilization of hides and skins. Research is, therefore, necessary to maintain the competitive position of leather and to find new outlets for animal hides.

The survival of leather in competition with synthetics lies in the retention of leather as a preferred material in the eyes of the consumer and hence it must be constantly developed and improved to retain that status. Though leather by itself has very desirable properties, there are a few drawbacks like weight and high water absorption in leathers which if removed will further enhance the usefulness of leather and improve its competitive position with respect to synthetics. By graft copolymerization it is possible to incorporate the polymers amidst hides, skins and leather, which may give them certain desirable qualities possessed by the synthetics. The appendage of side chains to protein fibres may result in the formation of composite macromolecules whose properties may differ from those of the original protein. Graft copolymerization thus yields a new tool to be used in the task of controlling and modifying molecular structure.

Summary

The various recently developed radiation and chemical techniques for grafting synthetic polymers (vinyl) to proteins are reviewed. The limitations of some of these methods are discussed. The main factors influencing the efficiency of graft copolymerization and the role of inhibitors and retarders are also discussed.

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